

Improvement of Hydrothermal Stability of MCM-41 Using Salt Effects during the Crystallization Process

Ryong Ryoo* and Shinae Jun

Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taeduk Science Town, Taejon, 305-701 Korea

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Low hydrothermal stability in hot water and aqueous solutions was a critical problem for many applications of the mesoporous molecular sieve MCM-41, compared with conventional zeolites such as Y and ZSM-5. The hydrothermal stability of MCM-41 has been found to improve remarkably by using various salts such as sodium chloride, potassium chloride, sodium acetate, and ethylenediaminetetraacetic acid tetrasodium salt during the hydrothermal crystallization process performed at 370 K. High-quality MCM-41 samples obtained by using the salt effect indicated negligible structural losses as judged by X-ray diffraction during heating for 12 h in boiling water.

1. Introduction

Recently, mesoporous molecular sieves designated MCM-41^{1,2} have attracted much attention because of their possible uses as supports for catalysts, hosts for the inclusion of compounds and nanosize clusters, and molecular sieves for large molecules. The structure of MCM-41 consists of parallel one-dimensional channels which form a hexagonal array. The significance of this material is due to its large channel diameter, ranging cross-sectionally from 1.6 to 10 nm compared with the channel diameters of crystalline microporous materials which are limited to below 2 nm. Further, the diameter of the MCM-41 channels can be tailored by using surfactants with different molecular sizes and auxiliary organic species during the crystallization process or suitable postsynthesis hydrothermal treatments. The large diameter of the channel and its tailorability provide new opportunities as supports for large chemical species and templates for nanosize architecture.^{3,4}

MCM-41 is reported to have high thermal stability and hydrothermal stability in air and oxygen containing water vapor. However, it has low hydrothermal stability in water and aqueous solutions.^{5–7} Chen et al.⁵ reported that pure-silica MCM-41 could be heated to 1123 K before structural collapse began. Kim et al.⁶ showed that the powder X-ray diffraction (XRD) pattern and BET surface area were not affected significantly by heating to 1170 K in air and O₂ containing water vapor up to 2.3 kPa. More recently, Kim and Ryoo⁷ reported that the mesoporous structure constructed with a pure-silica framework was stable in 100% steam flow under atmospheric pressure at 770 K. In contrast to such stability in air, O₂, and steam at high temperatures, MCM-41 was found to lose its structure during heating in boiling water and aqueous solutions.⁷ The structural loss involved silicate hydrolysis in water and aqueous solutions. These reports indicate that it is important to improve the hydrothermal stability of MCM-41, whereas applications such as exchanging cations,⁶ supporting metal clusters,⁸ and catalytic reaction⁹ in aqueous solutions can be limited by the structural disintegration.

The purpose of our research was to improve the weak hydrothermal stability of MCM-41. We have added various salts such as KCl, NaCl, sodium acetate, ethylenediaminetetra-

acetic acid tetrasodium salt (Na₄EDTA), K₄EDTA, and so on, into reaction mixtures during the hydrothermal crystallization of MCM-41, assuming that the salts can influence the structure of water and therefore the local structure of the silicate–surfactant mesostructures during the hydrothermal synthesis. In addition, we have investigated whether the salt effects can lead to a significant improvement of the hydrothermal stability of MCM-41.

2. Experimental Section

The hydrothermal crystallization procedures described in refs 2, 6, and 10 were used to obtain three pure-silica MCM-41 samples. The first sample was crystallized from a gel composition of 4SiO₂:1 hexadecyltrimethylammonium chloride (HTACl):1Na₂O:0.15(NH₄)₂O:200H₂O at 370 K, using sodium silicate as a silica source.^{6,10} The second sample was crystallized from a gel composition of 2SiO₂:[0.7HTACl + 0.3HTAOH]:52H₂O at 390 K by using tetramethylammonium silicate as a silica source.² The 0.7HTACl + 0.3HTAOH mixture was obtained by ion exchanging a 25 wt % aqueous solution of HTACl (Aldrich) with an anion exchange resin (SA 10A, Diaion) excessively and diluting with the HTACl solution. The third sample was synthesized by using the same gel mixture as the first sample. The gel mixture for the third sample was initially heated for 24 h at 370 K. After the reaction mixture was cooled to room temperature, acetic acid was added dropwise under vigorous stirring until the pH became 10.2. This mixture was heated again to 370 K for 24 h. The pH adjustment and subsequent heating were repeated twice more, in order to improve the long-range structural order and textural uniformity of the resulting MCM-41 product, following the method developed by Ryoo and Kim.^{6,10} All crystallized products were filtered, washed, dried, and calcined in the same ways reported previously.⁶

Hydrothermal stability of the above samples was investigated by following intensity changes in X-ray diffractograms as a function of the sample-heating times and temperatures in double-distilled water. The water to sample ratio was fixed as 1 L g⁻¹. In the case of heating at 373 K, the hydrothermal treatment was carried out under reflux conditions. At other temperatures, the treatment was carried out under static condition without agitation. After the hydrothermal treatment at given temperatures, samples were filtered, washed with double-distilled water,

* To whom correspondence should be addressed.

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and immediately placed in an oven to dry for 2 h at 400 K. XRD patterns were obtained at room temperature from the dried samples, with a Cu K α X-ray source using a Rigaku D/MAX-III (3 kW) instrument.

Magic angle spinning (MAS) ^{29}Si NMR spectra were obtained by using a Bruker AM 300 instrument with a relaxation delay of 5 s. Samples were spun at 3.5 kHz.

3. Results and Discussion

Structural Order and Physical Properties. A number of MCM-41 samples constructed with a silica framework was obtained in this research following three different preparation procedures. These samples showed significant differences in XRD peak intensity, resolution, and line width, depending on the details of the sample preparation procedures. XRD patterns of well-ordered samples had a very intense 100 diffraction peak and 3–5 additional higher-order peaks with weaker intensities. The high-order peaks showed no resolution or disappeared in other samples. In spite of such differences in the XRD pattern, all samples had very similar BET surface areas ranging from 800 to 1100 m 2 g $^{-1}$. The BET areas were not sensitive to the crystallization processes and silica sources used. Thus, the high-resolution XRD pattern was not an essential condition for the large surface area with MCM-41, which was consistent with previous reports.¹¹

In contrast to the surface area, pore size distribution for the MCM-41 samples varied widely, depending on the XRD line shape. The pore size was analyzed by using N $_2$ adsorption in this research following the Horvath–Kawazoe method.¹² Well-ordered samples exhibiting at least three X-ray diffraction peaks gave a narrow peak in the mesopore range of the pore size distribution. The peak width at half the full height for such well-ordered samples was as narrow as 3 nm. The peak width increased as the XRD peak resolution decreased, consistent with the peak widths above 10 nm for samples exhibiting only one diffraction peak in some previous studies.¹³

The low hydrothermal stability of MCM-41 in water and aqueous solutions has not been considered seriously in most studies reported in the literature to date. However, the low stability compared with conventional zeolites such as Y and ZSM-5 is a critical problem that affects the life of the material in applications requiring hot water and aqueous solutions in experimental conditions. For example, MCM-41 containing titanium in the framework was considered in previous reports as an excellent catalyst for partial oxidation of bulky organic compounds using an aqueous solution of H $_2$ O $_2$ as an oxidant. Nevertheless, the material was found to lose the catalytic activity after a few hours of use, due to structural disintegration in the aqueous solution.⁹ Low hydrothermal stability is also a difficult problem when transition metals and metal oxides such as Pt clusters⁸ and molybdenum oxides are to be incorporated by using hot aqueous solutions. Thus, the hydrothermal stability of MCM-41 is one of the most important physical properties that has to be considered for its future practical applications.

It is mentioned above that all highly ordered MCM-41 samples exhibited large surface areas and uniform pore sizes. If the hydrothermal stability of MCM-41 can also be correlated with the XRD line shape, such information will be extremely useful for the evaluation of the product quality with XRD. With this perspective in mind, various MCM-41 samples were obtained by following the crystallization procedures described in section 2. The samples were then heated in distilled water for 12 h at given temperatures. The resulting XRD patterns after the hydrothermal treatment are displayed relative to the heating temperatures in Figure 1. The XRD patterns for the calcined samples show a large variation in line width and

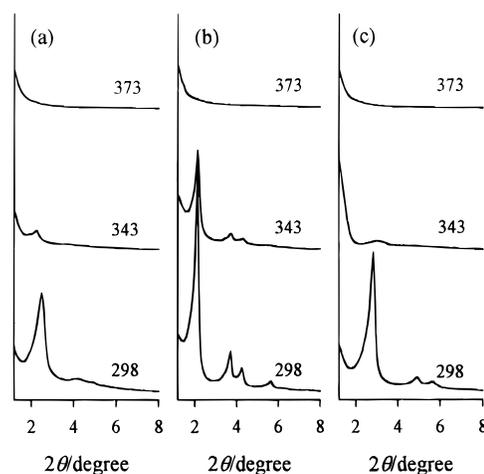


Figure 1. XRD patterns of MCM-41 after the samples were heated in distilled water for 12 h: (a, b) obtained from a molar composition of 4SiO $_2$:1HTACl:1Na $_2$ O:0.15(NH $_4$) $_2$ O:200H $_2$ O using sodium silicate as a silica source,^{6,10} and (c) obtained from 2SiO $_2$:[0.7HTACl + 0.3HTAOH]:52H $_2$ O using tetramethylammonium silicate as a silica source,² respectively. In contrast to no pH adjustment during the crystallization in (a) and (c), the pH was adjusted to 10.2 three times during the crystallization process in (b). The XRD patterns were obtained for dehydrated samples with a Cu K α X-ray source using a Rigaku D/MAX-III (3 kW) instrument. Numbers denote the heating temperatures in kelvin.

intensity. No significant changes occurred due to contact with water at room temperature. The XRD patterns decreased in intensity as the water temperature increased to 373 K, more or less depending on the details of the crystallization procedures. The decreases in XRD intensity are known to come from the disintegration of the MCM-41 structure in hot water and involve silicate hydrolysis, due to weak hydrothermal stability compared with zeolites such as NaY and ZSM-5.⁷

Among the three sample-preparation procedures used in this research to obtain pure-silica MCM-41, the procedure repeating the pH adjustment showed the best hydrothermal stability. Nevertheless, even the samples obtained following this procedure exhibited a loss of more than 30% in XRD intensity upon boiling in water for 1 h. Increasing the boiling time in water led to drastic decreases in the XRD intensity. The structural loss due to heating in water was much more serious for other samples. We have tried to find a correlation between the hydrothermal stability and the structural order of MCM-41. The high hydrothermal stability in Figure 1b compared with that in Figure 1a is concomitant with the improvement in the long-range structural order and textural uniformity. However, this relation fails when parts a and c of Figure 1 are compared.

Salt Effects on Hydrothermal Stability. It is reasonable that the formation of surfactant-silicate mesostructures from HTA $^+$ and a sodium silicate solution following the electrostatic templating route^{5,14} can be affected by the electrostatic interaction with ions constituting salts under high salt concentrations. Recently, Monnier et al.¹⁴ investigated the influence of the ionic strength on the surfactant-silicate assembly process by performing MCM-41 synthesis in a reaction solution containing 1 M NaCl. However, no salt effects were detected. The absence of salt effects in the study was perhaps due to a low concentration of salt. In fact, the addition of salt can either decrease or increase the hydrothermal stability of the calcined MCM-41 product very significantly, depending on the nature and the amount of salt and the addition time during the MCM-41 crystallization process. The salts' effects are presented in Figures 2–4.

Figure 2 and 3 display XRD patterns for products relative to the amounts of salt added to a reaction mixture during the

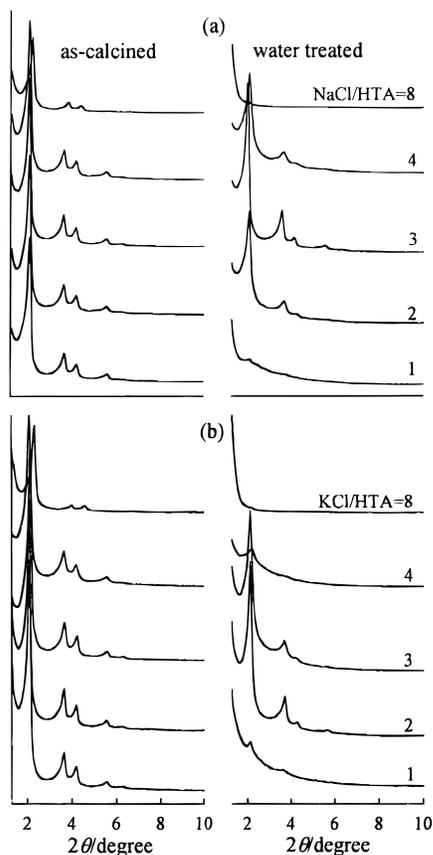


Figure 2. XRD patterns of MCM-41 displayed relative to the amounts of inorganic salts added to the synthesis gel mixtures: (a) NaCl and (b) KCl. The MCM-41 samples were crystallized from a molar composition of $4\text{SiO}_2:1\text{HTA}Cl:x\text{salt}:1\text{Na}_2\text{O}:0.15(\text{NH}_4)_2\text{O}:200+12x\text{H}_2\text{O}$ at 370 K, using sodium silicate as a silica source at 370 K. The pH was adjusted to 10.2 three times during the crystallization process. Numbers given to XRD patterns denote the salt-to-HTA molar ratio x . The salts were added after the first pH adjustment and subsequent heating period. The “water treated” data were collected after heating the calcined samples in boiling water for 12 h.

crystallization process of MCM-41. The MCM-41 samples were obtained by the same hydrothermal synthesis procedure, repeating the pH adjustment three times as described in section 2, except that various salts such as KCl, NaCl, sodium acetate, Na_4EDTA , and K_4EDTA were added. The salt was added to the reaction mixture at room temperature after the first pH adjustment and subsequently heated to 370 K for 24 h. The resulting mixture was heated again for 24 h at 370 K before being subjected to the second pH adjustment. The remainder of the procedure was the same as that described in section 2. The XRD patterns shown in Figures 2 and 3 were obtained after the resulting products were calcined and subsequently heated for 12 h in boiling water.

The MCM-41 structure obtained without salt was completely lost during the hydrothermal treatment for 12 h, as shown in Figure 1b. The addition of NaCl up to 3 mol/HTA caused the hydrothermal stability to increase very distinctly as the XRD patterns in Figure 2a show. When 3 moles of NaCl/HTA were used, the resulting MCM-41 structure showed no sign of disintegration during heating for 12 h in boiling water. However, the salt addition beyond 4 NaCl/HTA diminished the hydrothermal stability. The addition of up to 2 mol of KCl/HTA, 4 mol of sodium acetate, and 8 mol of Na_4EDTA led to a similar improvement of hydrothermal stability. These effects of salts on the hydrothermal stability of MCM-41 depended very dramatically on the concentration and the nature of the salts. The thermal stability of MCM-41 in O_2 was also improved along with the hydrothermal stability changes due to the salts' effects.

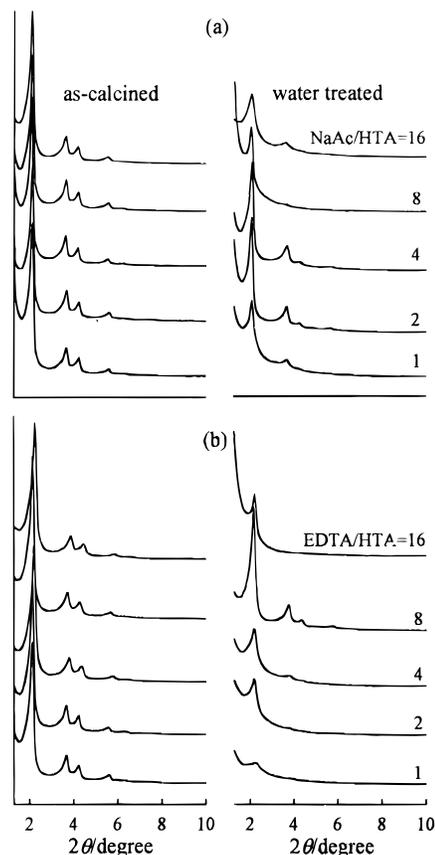


Figure 3. XRD patterns of MCM-41 obtained by using organic salts: (a) sodium acetate and (b) Na_4EDTA . The samples were obtained following the same procedure used in Figure 2.

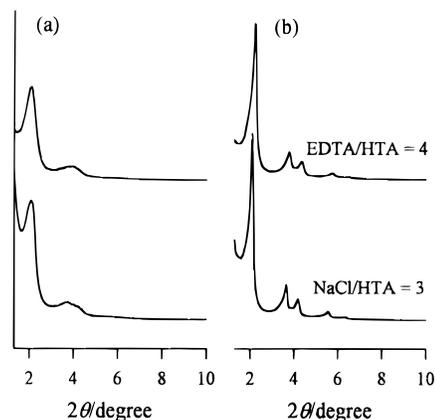


Figure 4. XRD patterns of calcined materials obtained from a gel composition of $4\text{SiO}_2:1\text{HTA}Cl:x\text{salt}:1\text{Na}_2\text{O}:0.15(\text{NH}_4)_2\text{O}:200+12x\text{H}_2\text{O}$ at 370 K, using sodium silicate as a silica source at 370 K. The salts (Na_4EDTA and NaCl) were mixed with HTA before the gel was heated to 370 K in (a), while the salts were added after the first pH adjustment and subsequent heating period in (b).

The XRD pattern of the sample obtained with 8 Na_4EDTA /HTA indicated no structural loss upon heating in an O_2 flow for 2 h at 1230 K, whereas the structure began to collapse at 1140 K without use of the salt effect.

In contrast to the addition of salts during the crystallization process, the addition of salts before heating the initial gel mixture to 370 K showed another type of interesting effect which caused systematic line broadening in the XRD, as shown in Figure 4. The resulting XRD patterns showed two or three very broad lines approximately equally spaced in the region of $2\theta = 2-8^\circ$. The specific surface area and pore size uniformity did not change significantly in spite of this broadening. Recently, it has been clarified that this XRD line broadening

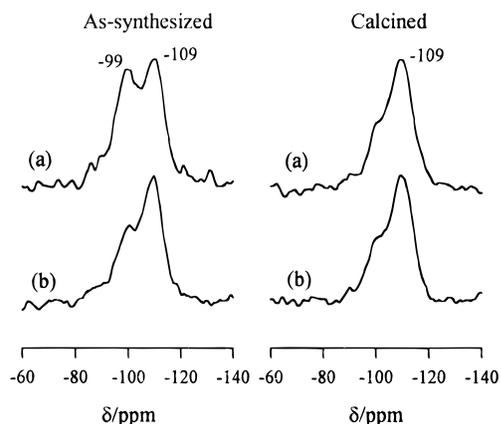


Figure 5. MAS ^{29}Si NMR spectra for MCM-41: (a) obtained from a molar composition of $4\text{SiO}_2:1\text{HTACl}:1\text{Na}_2\text{O}:0.15(\text{NH}_4)_2\text{O}:200\text{H}_2\text{O}$ at 370 K, and (b) obtained from $4\text{SiO}_2:1\text{HTACl}:8\text{Na}_4\text{EDTA}:1\text{Na}_2\text{O}:0.15(\text{NH}_4)_2\text{O}:300\text{H}_2\text{O}$. The pH was adjusted to 10.2 three times during the crystallization process. The Na_4EDTA was added after the first pH adjustment and subsequent heating period.

effect by salts comes from the formation of a disordered network of short wormlike mesoporous channels instead of the ordered MCM-41 structure.^{15,16}

The salt effects, depending on the mixing times, may be explained by using the concept of chemical potential. The chemical potential of a reaction mixture decreases as the reaction proceeds toward equilibrium. More specifically, the chemical potential of the MCM-41 synthesis reaction mixture can be assumed to decrease as the formation of the surfactant–silicate mesostructure proceeds. It is considered that a low chemical potential is obtained with the addition of the salts after the second heating step, compared with the initial mixing step where the formation of the surfactant–silicate mesostructure is not completed. If the salts are added to the initial gel mixture, the chemical potential of the reaction mixture obtained by the addition of the salts may be so high that the reaction exceeds the activation energy barrier from MCM-41 to the disordered surfactant–silicate mesostructures. It thus seems that the formation of the disordered mesostructures was prevented by adding the salts after the chemical potential decreased due to the complete formation of the surfactant–silicate mesostructure for MCM-41.

The salt effects for the improvement of hydrothermal stability of MCM-41 can be due to moderation of the electrostatic interaction between cationic surfactant micelles and surrounding silicate anions. The electrostatic interaction between the surface of the surfactant micelles and the silicates can be attenuated by the salt while the surfactant–silicate mesostructure is formed. It may be speculated that the silicates can be freed from strong electrostatic binding with the surfactant under such circumstances, and consequently the degree of silicate polymerization (i.e., silanol group condensation) is expected to increase, compared to a situation without such electrostatic attenuation.

MAS ^{29}Si NMR spectra are presented in Figure 5, in order to investigate the concentration of the remaining silanol groups after the formation of the mesostructure. The ^{29}Si NMR spectra for as-synthesized MCM-41 samples show a significant increase in the NMR peak ratio between $\text{Si}(\text{—OSi})_4$ tetrahedral silicon atoms and $\text{Si}(\text{—OSi})_3(\text{—OH})$ silicon atoms (i.e., Q^4/Q^3) due to the salt effect. Thus, the salt effect caused a decrease in the silanol group content for as-synthesized samples. The difference in silanol group concentration due to the salt effect disappeared when the samples were calcined. It is then reasonable to believe that excess silanol groups are forced to condense under calcination and the resulting structure has distortions in the Si—O—Si bond angles. Such a distorted structure seems to be

attacked readily by hydrolysis in hot water, compared with the structure obtained by using the salt effect.

It is also possible to speculate that the salt effect can influence the water structure, which determines the local structure of the surfactant–silicate mesostructure, improving hydrothermal stability. A similar role of water molecules has been reported recently by Emmer and Wiebcke¹⁷ for three-dimensional heteronetwork channel structures formed with oligomeric silicate anions, water, and quaternary organic amines. The crystal structures showed water molecules forming hydrogen bonding between silicates and amines. It may be assumed that hydrothermal crystallization of MCM-41 exhibits common structural features with the heteronetwork channel structures under similar crystallization conditions. In this case, the local structure of the resulting MCM-41 product can also be affected by the local structure of water on the molecular level.

4. Conclusion

It is shown in this work that the hydrothermal stability of MCM-41 after calcination can be improved remarkably by using salt effects during the hydrothermal crystallization process. MCM-41 materials obtained by using the salt effect were stable for at least 12 h in boiling water under reflux conditions. The stabilization of the MCM-41 structure using the salt effect can make a significant contribution to solving critical problems associated with weak hydrothermal stability of the mesoporous material compared with conventional zeolites such as Y and ZSM-5. It is also expected that the salt effect can be useful for the stabilization of the structures of other mesoporous molecular sieves that can be synthesized under conditions similar to those of MCM-41. More detailed information on the local structure of MCM-41 would be necessary to understand the role of the salt on the molecular level during the crystallization.

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